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Microstructure and kinetics of formation of Si_2N_2O and Si_3N_4 into Si porous preforms by chemical vapor infiltration (CVI)

J.L. de la Peña, M.I. Pech-Canul *

Centro de Investigación y de Estudios Avanzados del IPN, Unidad Saltillo, Carretera Saltillo,
Monterrey Km. 13, Saltillo Coahuila México 25900, Mexico

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Abstract

The kinetics of formation of Si_2N_2O and Si_3N_4 into Si porous preforms via chemical vapor infiltration (CVI) in N_2 and N_2–5% NH_3, has been investigated. In addition, the effect of the following processing parameters on the phase, amount and product morphology was investigated: atmosphere, time, temperature, gas flow rate, particle size and porosity of Si porous preforms. A Taguchi experimental design allowed establishing that atmosphere is the parameter that most significantly influences the type of phase formed and that processing time and temperature are the parameters that most significantly affect the amount and morphology of the phases formed. In nitrogen Si_2N_2O is formed primarily with morphology of whiskers and fibers which grow with time and temperature. In N_2–5% NH_3, Si_3N_4 is formed predominantly in the form of coatings on the Si particles. Although thermodynamically, the reaction for formation of Si_2N_2O is more feasible than that for Si_3N_4, kinetically the reaction for formation of the latter occurs faster. The activation energy (E) for the reaction with pure N_2 is 88.3 kJ/mol while the corresponding value for the reaction with N_2–5% NH_3 is 48.3 kJ/mol.

Keywords: A. Powders: gas phase reactions; B. Porosity; B. Whiskers; D. Si_3N_4

1. Introduction

Porous ceramics are attractive materials for a wide variety of technological applications including molten metal filters, catalyst supports, radiant burners and preforms for the production of metal/ceramic composites by the melt infiltration route [1,2]. The major requirements for these applications are that the materials possess high temperature stability, excellent thermal shock resistance and resistance to chemical attack. A variety of potential materials can be considered to produce porous ceramic materials, including silicon carbide, alumina, boron nitride, silicon nitride and oxynitride.

Silicon nitride (Si_3N_4) and silicon oxynitride (Si_2N_2O) are strong candidates for producing porous materials because of their attractive properties. The former has an exceptional wear and corrosion resistance and high-temperature mechanical properties. Due to its low thermal expansion coefficient and high thermal conductivity, Si_3N_4 has excellent thermal shock resistance [3]. Silicon oxynitride (Si_2N_2O) offers superior chemical and oxidation resistance in many environments at high temperatures [4,5]. The most common applications for Si_2N_2O reported in the literature include cutting tools, wear parts and heat engine components. However, its use has been limited due to barriers associated to synthesis and densification [5].

The conventional routes for synthesis of Si_3N_4 powders such as the carbothermic reduction of SiO_2 and the direct nitridation of silicon powders entail solid–gas reactions in the temperature range 1473–1823 K [3]. However, some disadvantages related to the presence of impurities in the products have motivated the use of gas phase processing methods, like the chemical vapor deposition (CVD) route. Moreover, the gas phase routes allow producing Si_3N_4 with a variety of morphologies, including fine powders, single-crystals/polycrystals, whiskers/fibers and films/coatings [6,7]. Although silicon chloride ($SiCl_4$) is one of the most common silicon precursors for the synthesis of Si_3N_4 by CVD, the use of silicon tetrafluoride (SiF_4) has also been considered in the last years [8–11]. Indeed, it has been reported that $SiCl_4$ tends to polymerize and clog the exit port of the reactors

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* Corresponding author. Tel.: +52 844 4 38 9600; fax: +52 844 4 38 9610.
E-mail address: martin.pech@cinvestav.edu.mx (M.I. Pech-Canul).

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[8]. It is noteworthy that in the conventional CVD systems, the silicon precursors ($SiCl_4$, SiF_4 and SiH_4) are normally supplied to the reactors from an external gas container [8,9].

Due to the growing interest in the production of Si_3N_4 for a variety of applications, alternative processing methods as the combustion synthesis route (CS), the reaction of Mg_2Si with NH_4Cl and the reaction of $SiCl_4$ with NaN_3, have been developed in recent years [12–15]. The synthesis of Si_3N_4 fibers through the CS route in nitrogen was reported by Rodriguez et al. [12] and Cao et al. [13]. In the work by Rodriguez et al., the use of high pressures of nitrogen (12 MPa) for the production of β-Si_3N_4 fibers seemed to be a process drawback. This problem was overcome later by Cao et al. by using lower nitrogen pressures (0.5–1 MPa); however, they also used sodium azide (NaN_3) as a catalyst for the growth of Si_3N_4 whiskers. Unfortunately, like most of the azides, NaN_3 is an unstable substance highly sensitive to shock, used in the manufacture of explosives; therefore, cost and handling difficulties may cause inconveniences to its use. In addition, apparently, these particular processes are limited to the production of Si_3N_4 only with the morphology of whiskers/fibers. The routes involving the reactions with NH_4Cl and $SiCl_4$ also have the inconvenient of high processing pressures (30–40 MPa) and the latter also uses NaN_3 [14,15]. Recently, in the work by Leal-Cruz, SiF_4 obtained from the thermal decomposition of sodium hexafluorosilicate (Na_2SiF_6) was used to produce Si_3N_4 in an in situ mode through gas phase reactions in nitrogen containing atmospheres at pressures slightly above to that of the atmospheric pressure and temperatures up to 1573 K [10,11]. The use of Na_2SiF_6 as a silicon solid precursor allows producing fine powders, whiskers/fibers and coatings.

A variant of the CVD method, referred to as chemical vapor infiltration (CVI) allows the deposition of new phases by the transport of gas precursors through a porous ceramic body, usually known as the preform. During the CVI process, the gaseous reactants diffuse and infiltrate through the porous structures where the gas-reactants undergo decomposition and chemical reactions to deposit the phase of interest on the surface of the constituents (fibers, particles) in the preform [16]. Although one of the most common procedures for producing porous materials is the impregnation of polyurethane sponge with slurries, the chemical vapor infiltration (CVI) route also offers the potential for producing porous structures. Furthermore, depending on the processing parameters, dense bodies for use in a variety of applications may be produced. In this work, the kinetics of formation of Si_2N_2O and Si_3N_4 into Si porous preforms via CVI during the thermal decomposition of Na_2SiF_6 has been investigated. In addition, the effect of the processing parameters on the type of phase, amount and product morphology was studied.

2. Experimental procedures

A Taguchi experimental design L_{32} was used to investigate the effect of the processing parameters on the type (Si_3N_4 and Si_2N_2O), amount and morphology of phases formed and deposited into silicon porous preforms. Table 1 shows the parameters and levels tested in the experiment. Predetermined amounts of commercial silicon powders were used to prepare by uniaxial compaction, cylindrical preforms (3 cm in diameter × 3 cm high) with the characteristics given in Table 1. Similarly, an amount of 20 g of powders of the salt Na_2SiF_6 was used to prepare cylindrical compacts (3 cm in diameter × 4 cm long) with 60% porosity.

Table 1
Parameters and levels tested in the L_{32} Taguchi experiment design

No.	*t* (min)	*T* (K)	Flow rate (cm^3/min)	*P* (%)	PS (μm)
L_1	30	1273	46.5	40	20
L_2	30	1373	93	50	40
L_3	30	1473	120.2	60	60
L_4	30	1573	240.4	70	80
L_5	60	1273	46.5	50	60
L_6	60	1373	93	40	80
L_7	60	1473	120.2	70	20
L_8	60	1573	240.4	60	40
L_9	90	1273	93	70	20
L_{10}	90	1373	46.5	60	40
L_{11}	90	1473	240.4	50	60
L_{12}	90	1573	120.2	40	80
L_{13}	120	1273	93	60	60
L_{14}	120	1373	46.5	70	80
L_{15}	120	1473	240.4	40	20
L_{16}	120	1573	120.2	50	40
L_{17}	30	1273	240.4	70	40
L_{18}	30	1373	120.2	60	20
L_{19}	30	1473	93	50	80
L_{20}	30	1573	46.5	40	60
L_{21}	60	1273	240.4	60	80
L_{22}	60	1373	120.2	70	60
L_{23}	60	1473	93	40	40
L_{24}	60	1573	46.5	50	20
L_{25}	90	1273	120.2	40	40
L_{26}	90	1373	240.4	50	20
L_{27}	90	1473	35	60	80
L_{28}	90	1573	93	70	60
L_{29}	120	1273	120.2	50	80
L_{30}	120	1373	240.4	40	60
L_{31}	120	1473	46.5	70	40
L_{32}	120	1573	93	60	20

P: silicon preform porosity; PS: silicon particle size in the preform.

Chemical vapor infiltration trials were performed in a reactor consisting of a horizontal alumina-tube furnace (3.1 cm in diameter × 76 cm long) provided with end-cap fittings to control the process atmosphere. The silicon preforms were placed in the center of the reactor and the Na_2SiF_6 compacts were positioned nearby the gas entrance, where the temperature is in the range 573–623 K [10,11]. According to Table 1, the specimens were heated in the corresponding atmosphere at a rate of 15 °C/min up to the test temperature and then maintained at this temperature for a given test time. It is noteworthy that the programmed test temperatures match with temperatures in the center of the tube, which correspond to the hot zone of the reactor. The molar ratio levels of N_2 and SiF_4 were established according to the rate of the thermal decomposition of Na_2SiF_6 and the gas by-products were made to bubble into a deposit containing distilled water. Throughout the trials the reactor was maintained at a constant pressure,

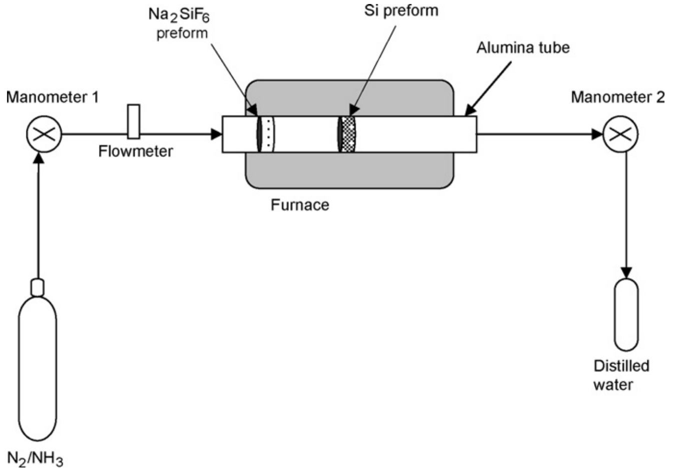

Fig. 1. Schematic representation of the experimental set-up [10,11].

which is slightly above to that of the atmospheric pressure (gage pressure: 8 ± 1 mbar) and the temperatures of the Si preforms and salt-compacts were monitored using K-type thermocouples. Fig. 1 is a schematic of the experimental set-up used in the investigation. After cooling to room temperature the infiltrated specimens were removed from the furnace for characterization. The total amount of phases deposited into the preforms was determined gravimetrically and the microstructural characterization was carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

3. Results and discussions

3.1. Effect of processing parameters on the type of phases formed

Results from XRD and SEM reveal that Si_3N_4 as well as Si_2N_2O were formed in both, nitrogen and nitrogen-5% ammonia atmospheres. However, while in pure nitrogen the phase predominantly formed is Si_2N_2O, in nitrogen–ammonia Si_3N_4 was the favored compound. In Fig. 2, XRD patterns of specimens tested in N_2 are shown. At medium and high levels of temperature and time, only silicon oxynitride is detected as a new phase. Indeed, silicon Si_3N_4 is revealed only in specimens processed at 1573 K for 120 min (trial L_{16}).

In N_2–5% NH_3, Si_3N_4 starts appearing at intermediate temperatures and times and with higher intensities. Moreover, the higher the temperature and time the higher the tendency for formation of exclusively Si_3N_4. In Fig. 3, XRD patterns of specimens tested in N_2–NH_3 are shown. A qualitative comparison of the XRD patterns from trials L_{16} and L_{32} shows that in N_2–5% NH_3 the selective production of Si_3N_4 is favored. Moreover, under the conditions of trial L_{32}, Si_3N_4 is formed both in the α and β polymorphs. A comparison of the results from specimens L_{12} and L_{28}, tested under the same conditions but in different atmospheres shows that an addition of 5% ammonia to nitrogen triggers formation of Si_3N_4 at lower temperatures and times.

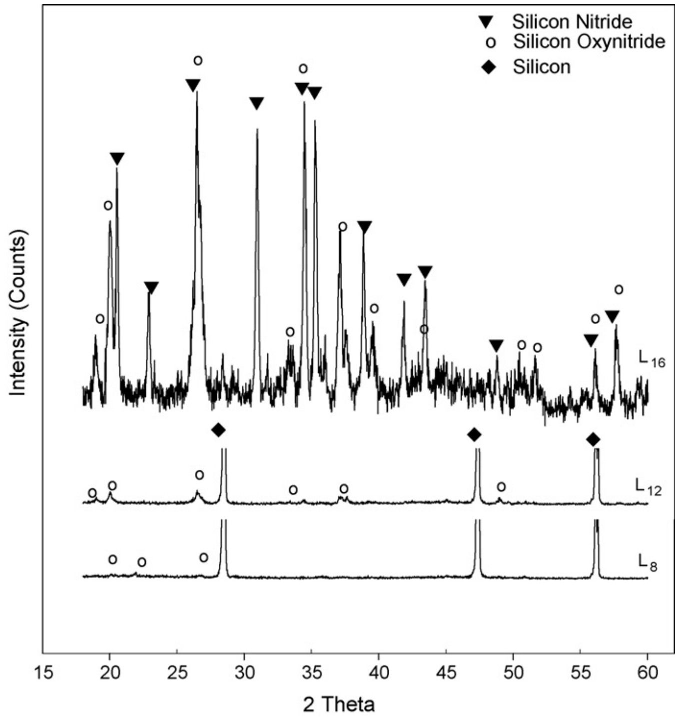

Fig. 2. XRD patterns from specimens tested in N_2 atmosphere.

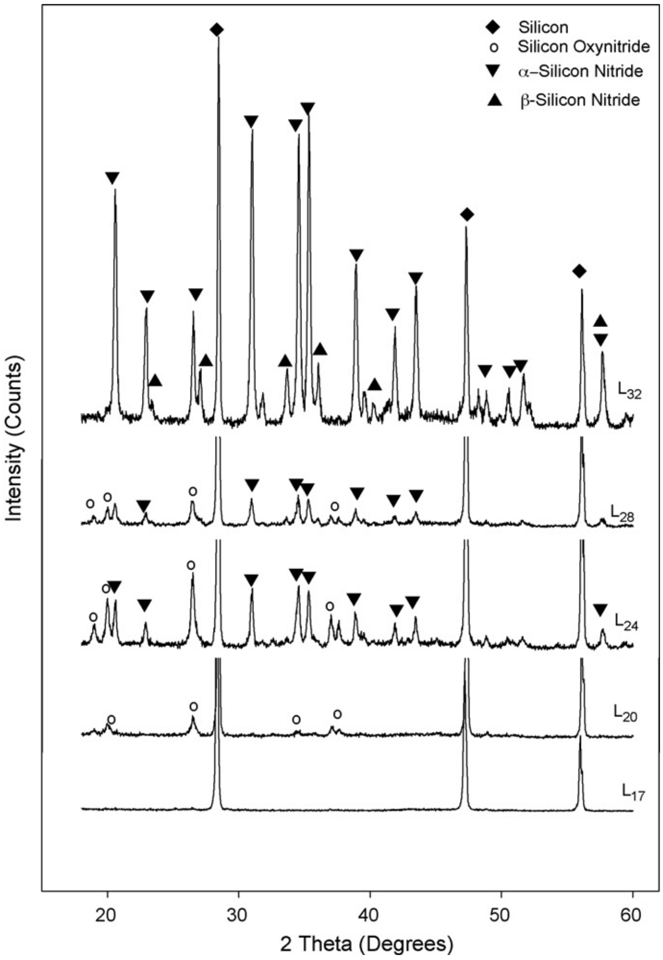

Fig. 3. XRD patterns from specimens tested in N_2–5% NH_3 atmosphere.

Silicon nitride can be formed according to the following reactions:

$$3SiF_4(g) + 2N_2(g) \rightarrow Si_3N_4(s) + 6F_2(g) \quad (1)$$

$$3SiF_4(g) + N_2(g) + 2NH_3 \rightarrow Si_3N_4(s) + 6HF + 3F_2(g) \quad (2)$$

A plot of the Gibbs free energy as a function of temperature for the reactions of silicon tetrafluoride (SiF_4) with N_2, NH_3 and N_2–NH_3 shows the benefits of adding ammonia to the atmosphere of pure nitrogen (see Fig. 4).

Formation of silicon oxynitride can be explained according to three possibilities. The first one is related to the oxidation of the Si_3N_4 formed in accordance with reactions (1) and (2):

$$2Si_3N_4(s) + (3/2)O_2(g) \rightarrow 3Si_2N_2O(s) + N_2(g) \quad (3)$$

Under normal oxygen pressures, Si_3N_4 is thermodynamically unstable with respect to oxidation. Even though it has excellent high-temperature mechanical properties, suffers from poor oxidation resistance at high temperatures. Moreover, although thermodynamically reaction (3) is highly feasible (for instance, at 1500 K, $\Delta G_R = -1063$ kJ/mol), the oxidation of Si_3N_4 occurs slowly, following approximately a kinetics with parabolic behavior [17]. Once oxidation has occurred, the oxide film formed serves as a protection against catastrophic oxidation by precluding the transport of oxygen atoms through the nitride surface. In fact, passive oxidation and the ability of Si_3N_4 to resist high temperatures under oxidizing conditions rely on the integrity and stability of the oxide layer in the surface. The second possibility is the direct nitridation of silicon in the porous preforms by the diffusion of nitrogen atoms into the native SiO_2 layer of Si. The thermal nitridation of ultrathin SiO_2 films in NH_3 has been reported previously by Jintsugawa et al., suggesting that due to the reaction with ammonia, the nitrogen species are adsorbed at the outermost SiO_2 surface, diffuse into the SiO_2 film and then nitride the Si substrate surface at the SiO_2/Si interface [18].

The third alternative involves the reaction of SiF_4 with nitrogen and oxygen in the atmosphere, in accordance with the following reaction:

$$6SiF_4(g) + (3/2)O_2(g) + N_2(g) \rightarrow 3Si_2N_2O(s) + 12F_2(g) \quad (4)$$

Due to the lack of thermodynamic data, the Gibbs free energy for reaction (4) was calculated only at the temperature of 1500 K. According to Fig. 4, it is evident that the reactions of SiF_4 with nitrogen or nitrogen–ammonia are much less thermodynamically feasible than reaction (4). Since oxidation of Si_3N_4 occurs slowly and formation of Si_2N_2O via diffusion of oxygen atoms through the silica layer of Si involves NH_3, it is improbable that the Si_2N_2O detected in the specimens treated in N_2 was formed by the oxidation of Si_3N_4 during the cooling event or by nitridation of SiO_2. Rather, it is most likely that it was formed through reaction (4). The oxygen involved in reaction (4) comes from the ultra high purity (UHP) N_2 as an impurity. According to these results, traces (<5 ppm) of oxygen (as O_2 or H_2O) are sufficient to produce silicon oxynitride via reaction (4).

3.2. Effect of processing parameters on the product morphology

Results from the analysis by SEM of specimens processed in N_2 reveal that Si_2N_2O whiskers are predominantly deposited

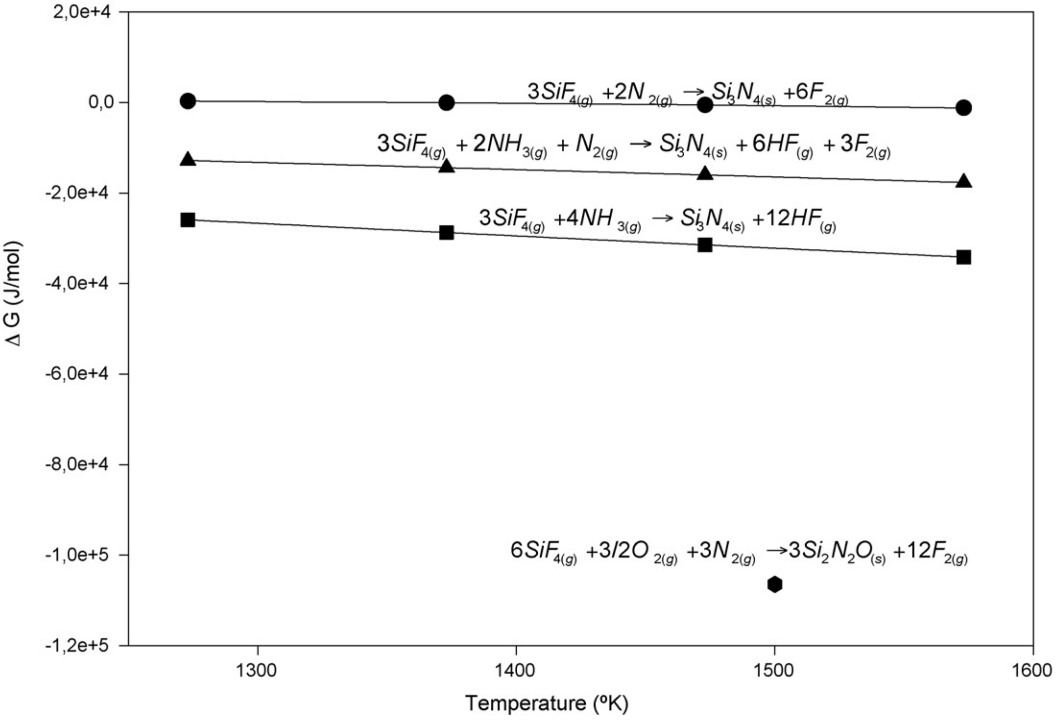

Fig. 4. Gibbs free energy plots of reactions involving SiF_4, N_2 and N_2–NH_3 as a function of temperature.

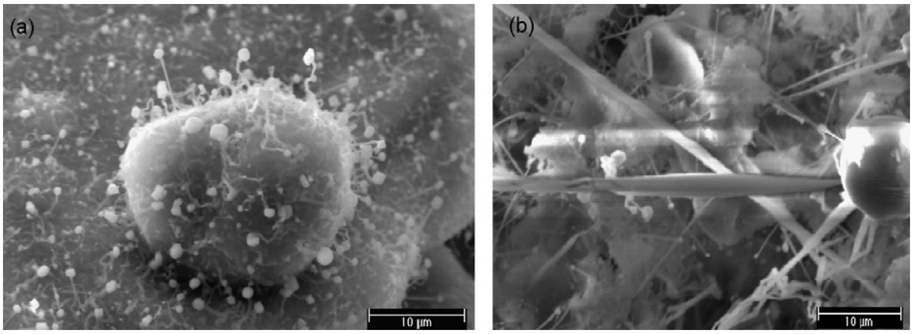

Fig. 5. SEM photomicrographs showing Si_2N_2O whiskers and fibers grown in N_2.

into the interstices of the silicon preforms and that although both, processing time and temperature have a notable influence, temperature is the parameter that most significantly affects the amount, size and product morphology. In addition, with increase in time and temperature, the whiskers tend to grow and the preforms become denser. An increase in temperature and time from 1373 to 1473 K and from 30 to 120 min processing time respectively, promotes a change in the Si_2N_2O morphology from whiskers to fibers. This can be observed in Fig. 5 from micrographs of L_2 and L_{15} specimens.

As shown in Fig. 6 in micrographs of specimens from trials L_7 and L_8, a variation in temperature from 1473 to 1573 K, at a constant processing time of 60 min results in a modification in the morphology of Si_2N_2O from thin to thick coatings on the Si particles.

In N_2–5% NH_3, Si_2N_2O and Si_3N_4 are deposited on the Si particles in both morphologies (whiskers/coatings) but mainly as coatings. In Fig. 7, SEM photomicrographs of specimens from trials L_{20} and L_{24} are shown. At constant temperature (1573 K) and gas flow rate (46.5 cm^3/min), but with variation in the processing time from 30 to 60 min, formation of Si_3N_4 is activated. As illustrated in Fig. 7, the Si_2N_2O and Si_3N_4 coatings become denser when the processing time is prolonged to 60 min. With increase to the highest levels of temperature and time, formation of silicon nitride is primarily favored and an augment in the densification of the preforms is observed. This is shown in Fig. 8 from micrographs obtained in specimens L_{28} and L_{32}. The tendency for formation of either whiskers/fibers or coatings of fine powders is related to the concentration (supersaturation) of adsorbed atoms or molecules of the new

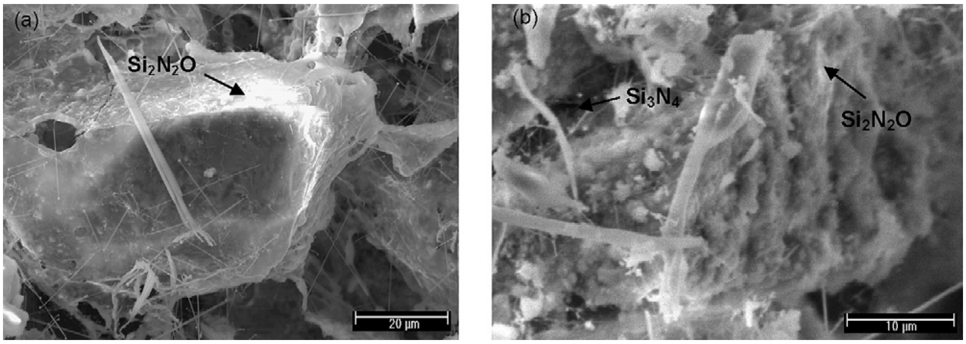

Fig. 6. SEM photomicrographs showing thin and thick Si_2N_2O coatings grown for 60 min at: (a) 1473 °C and (b) 1573 °C, respectively.

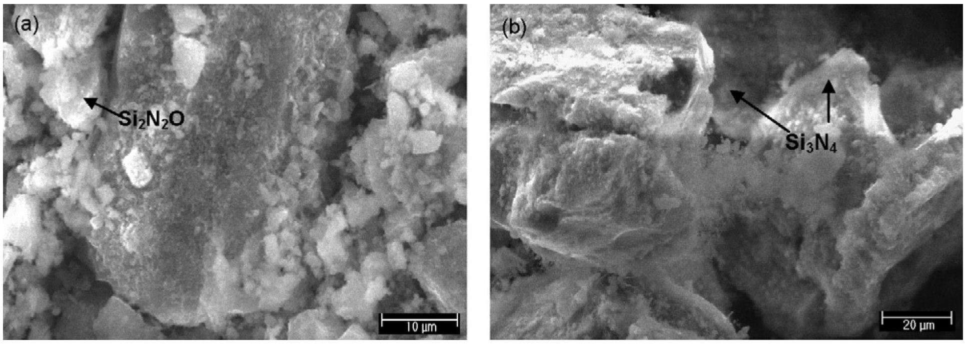

Fig. 7. SEM photomicrographs showing Si_2N_2O and Si_3N_4 coatings deposited in N_2–5% NH_3 at 1573 °C, using a gas flow rate of 46.5 cm^3/min for: (a) 30 min and (b) 60 min.

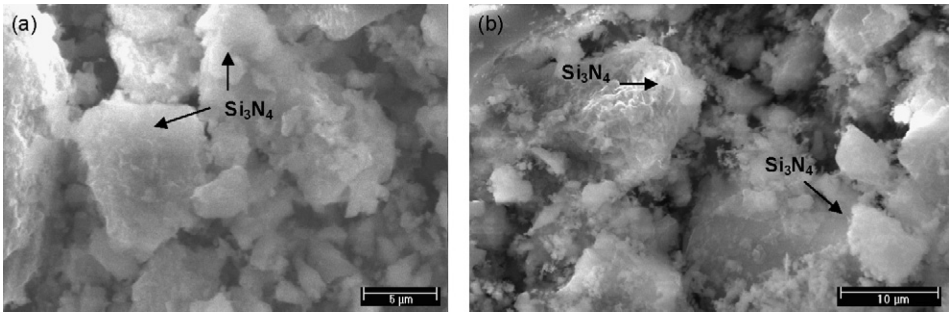

Fig. 8. SEM photomicrographs showing Si_3N_4 coatings deposited in N_2–5% NH_3 at 1573 °C for: (a) 90 min and (b) 120 min.

phase on the substrate surface. Typically by the CVD processes, whiskers are formed at low levels of supersaturation and high temperatures, while fine powders (polycrystals) are favored at medium temperatures and high supersaturation levels [19].

3.3. Effect of processing parameters on the amount of phases formed

The total amount of phases formed during the tests was determined measuring the weight gain of the infiltrated specimens. Fig. 9 is a chart of the weight gain (%) in the Si preforms for all the 32 tests. A simple comparison shows that in N_2–5% NH_3 the weight of the preforms increased up to 18% while in nitrogen the highest weight gain was of 12%. The increase in the amount of Si_3N_4 and Si_2N_2O formed and deposited when ammonia is present can be explained in the light of the thermal and chemical stability of NH_3 in comparison to that for N_2. Specifically, the ionization potential for NH_3 is 10.2 eV while the corresponding value for N_2 is 15.576 eV [20]. Furthermore, it can also be attributed to the strength of the bonds in nitrogen and ammonia. At 298 K, the strengths of the H–N and N–N bonds are 75 and 226.8 kcal/mol, respectively [21].

In order to determine the effect of the processing parameters on the amount of Si_3N_4 and Si_2N_2O formed together into the silicon preforms, analysis of variance (ANOVA) was performed. Analysis of variance provides insight into the optimum process parameters and allows estimating the amount of phases formed when using the optimum process parameters [22]. In addition, ANOVA provides a means of estimating the percent contribution of each of the parameters tested to the variability in the measured quantities. In accordance with Table 2, the parameter that most significantly affects the variability in the amount of phases formed is the temperature, with a relative contribution of 46.5%, followed by processing time, with a relative contribution of 24% and by the process atmosphere with 8.5%. The effect of Si particle size, preform porosity and gas flow rate is insignificant. Table 3 contains the optimum conditions to maximize the amount of deposited phases (Si_3N_4 and Si_2N_2O) into the silicon preform, obtained from the analysis of variance. Verification trials conducted under the conditions given in Table 3 allowed obtaining specimens with an average weight gain of 21%. Although apparently, preform porosity, silicon particle size and gas flow rate do not have important effects on the amount of phases formed, the optimization analysis revealed that the amount of phases deposited is enhanced if the preforms have a porosity of 50% with a Si particle size of 20 μm, and if infiltration is carried out with a gas flow rate of 120 cm^3/min. These results can be explained as follows. High levels of porosity in the preforms permit that the reactants and/or products pass through the interstices of the porous structures, especially at high gas

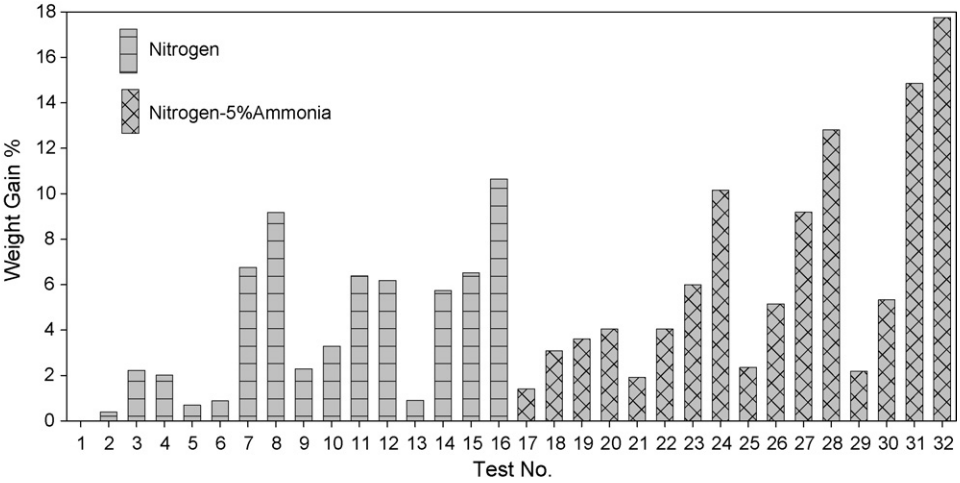

Fig. 9. Chart of the weight gain (%) in the Si preforms for all the 32 tests.

Table 2
ANOVA table for the amount of silicon nitride and oxynitride formed

Factors	d.f.	SS	MS	*F*	*P* (%)
Atmosphere	1.00	52.17	52.17	13.29	8.50
Time	3.00	149.92	49.97	12.73	24.00
Temperature	3.00	288.38	96.13	24.49	46.50
Porosity	3.00	10.72	3.57	0.91	2.00
Particle size	3.00	30.45	10.15	2.59	5.00
Flow rate	3.00	28.47	9.49	2.42	4.50
Error	15.00	58.88	3.93	–	9.50
Total					100.00

d.f.: degrees of freedom; SS: sum of squares; MS: mean of squares; *F*: variance ratio; *P*: percentage of contribution.

Table 3
Optimum conditions for maximizing the amount of phases formed

Factor	Level
Atmosphere	N_2–5% NH_3
Time	2 h
Temperature	1573 K
Porosity	50%
Si particle size	20 μm
Gas flow rate	120.4 cm^3/min

flow rates, thus decreasing the efficiency of deposition. Besides, nucleation of Si_3N_4 is enhanced with a decrease in particle size. Therefore, high levels of porosity in the preforms, high flow rate levels and large Si particle sizes are non-ideal parameters for deposition by CVI of the phases formed.

3.4. Kinetics of reactions for formation of Si_2N_2O and Si_3N_4

The study on the kinetics of the reactions was carried out under the following considerations: (a) the weight gain in the specimens tested in pure N_2 is due only to Si_2N_2O and in N_2–NH_3 the weight increase is attributed only to Si_3N_4; (b) a reacting system with constant volume, pressure and temperature; (c) the reactions for formation of both phases are simple, that is, each one of them can be represented by only one stoichiometric reaction and one velocity equation. The reactions considered for formation of Si_3N_4 and Si_2N_2O are given in Eqs. (2) and (4), correspondingly. The total molar quantity of each phase was determined from the weight gain of the silicon preforms plus the amount of products collected in a container installed after the port exit (product trap). Figs. 10 and 11 are plots of the amount of Si_2N_2O and Si_3N_4 formed (in mol%) as a function of time for various temperatures, respectively. In nitrogen, a significant increase in the formation of Si_2N_2O is observed when the temperature is varied from 1373 to 1473 K.

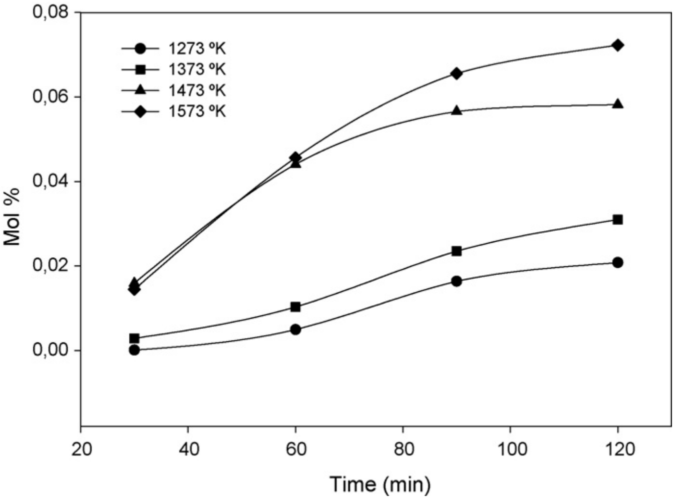

Fig. 10. Plots of mol% as a function of time for various temperatures from tests conducted in N_2.

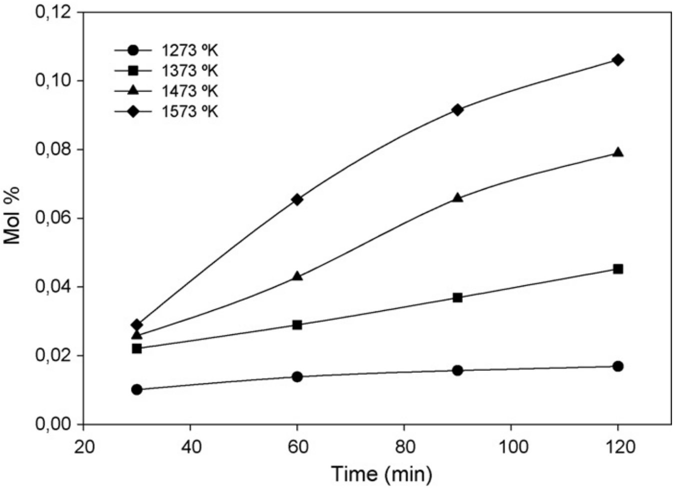

Fig. 11. Plots of mol% as a function of time for various temperatures from tests conducted in N_2–5% NH_3.

Simple models were considered in the analysis for the determination (by the differential method) of the magnitude of the order of reactions and rate constants:

$$\frac{\partial C_{Si_3N_4}}{\partial t} = k_1 C_{Si_3N_4}^{n_1} \tag{5}$$

$$\frac{\partial C_{Si_2N_2O}}{\partial t} = k_2 C_{Si_2N_2O}^{n_2} \tag{6}$$

where k_1 is the constant of reaction for Si_3N_4, k_2 the constant of reaction for Si_2N_2O, n_1 the order of reaction for Si_3N_4, n_2 the order of reaction for Si_2N_2O; $C_{Si_2N_2O}$ and $C_{Si_3N_4}$ are the molar concentrations of Si_2N_2O and Si_3N_4, respectively. The orders and constants of reactions determined are summarized in

Table 4
Variation with temperature of orders of reaction and reaction rate constants

Atmosphere	1273 K	1373 K	1473 K	1573 K
Nitrogen				
Order of reaction (n_2)	0.99	0.97	0.9	0.89
Constant of reaction (k_2) (min^{-1})	6.58E−05	1.14E−04	1.82E−04	3.0E−04
N_2–5% NH_3				
Order of reaction (n_1)	0.4	0.38	0.37	0.33
Constant of reaction (k_1) (min^{-1})	7.45E−04	1.04E−03	1.38E−03	1.78E−03

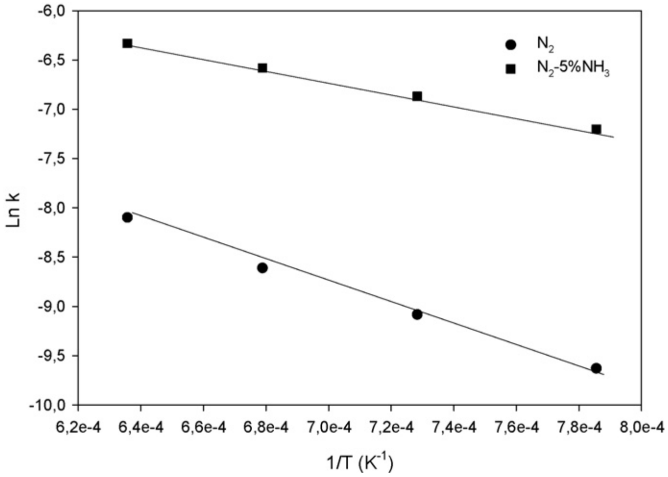

Fig. 12. Arrhenius plots for reactions in N_2 and N_2–5% NH_3.

Table 4. The effect of temperature on the reaction rate constant is given by the activation energy, which is calculated using the Arrhenius equation:

$$k = k_0\,\mathrm{e}^{-E/RT} \qquad (7)$$

where E is the activation energy, k_0 the pre-exponential factor, R the gas constant and T is the absolute temperature. According to the Arrhenius plots, shown in Fig. 12, the activation energies (E) for reactions (2) and (4) are 88.3 and 48.3 kJ/mol, respectively. Although thermodynamically, the reaction for formation of Si_2N_2O is more feasible than that for Si_3N_4, results from this work suggest that kinetically, the reaction for formation of silicon nitride occurs faster than reaction (4).

4. Summary and conclusions

Silicon nitride and oxynitride have been synthesized by the reaction of silicon tetrafluoride (SiF_4) with N_2–5% NH_3 and N_2 respectively, and deposited into Si preforms via chemical vapor infiltration (CVI). The Si precursor (SiF_4) is formed in situ during the thermal decomposition of sodium hexafluorosilicate (Na_2SiF_6). It was found that the processing atmosphere is the parameter that most significantly affects the phase produced (Si_2N_2O or Si_3N_4). While in nitrogen, formation of Si_2N_2O is preferentially promoted, in N_2–5% NH_3, the production of Si_3N_4 is predominantly favored. Although both, whiskers and coatings are produced in nitrogen, whiskers are preferentially formed. By contrast, in the ammonia containing atmosphere, coatings on the Si particles are mainly produced. The whiskers/fibers and coatings produced in both atmospheres are observed to grow with time and temperature. Although thermodynamically, formation of Si_2N_2O is more spontaneous, in the presence of 5% ammonia, kinetically formation of Si_3N_4 results favored. The activation energy for formation of Si_2N_2O is 88.3 kJ/mol and the corresponding value for Si_3N_4 production is 48.3 kJ/mol.

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